Structure of Si(111)-In Nanowires Determined from the Midinfrared Optical Response

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The anisotropic optical response of Si(111) − (4 × 1)/(8 × 2)-In in the midinfrared, where *ab initio* studies predict significant changes in the band structure between competing models of this important quasi-1D system, has been measured using infrared spectroscopic ellipsometry (IRSE) and reflection anisotropy spectroscopy (RAS). Both IRSE and RAS of the (8 × 2) phase show that the anisotropic Drude tail of the (4 × 1) phase is replaced by two peaks at 0.50 and 0.72 eV, which appear in *ab initio* optical response calculations for the hexagon model of the (8 × 2) structure, but not the trimer model.

One-dimensional (1D) electronic systems are attracting considerable interest for both fundamental and technological reasons. Fascinating phenomena, such as spin-charge separation [1], and charge-density wave (CDW) formation due the Peierls instability may appear, while quasi-1D structures are being investigated as atomic-scale interconnects in devices. Such structures can be grown by self-assembly on Si surfaces [2], where the existence of an energy gap prevents the coupling of the electronic states of the nanostructure with the substrate in the vicinity of the Fermi level, thus preserving the quasi-1D character of the nanostructure states.

An intensively studied model system is the ordered array of In nanowires that self-assembles at the Si(111) surface to form the Si(111)-(4 × 1)-In phase, which has quasi-1D metallic properties at room temperature (RT). Results from many different experiments, as well as *ab initio* band structure calculations, agree that the structure is metallic, with the In atoms forming two parallel zigzag chains, which are separated by zigzag Si chains that resemble the π-bonded chains of Si(111)-(2 × 1) [3–14]. The structure has three quasi-1D surface state bands, which disperse strongly and cross the Fermi level along the chain direction, and show only a weak dispersion perpendicular to the chain.

Yeom *et al.* [15] reported that Si(111)-(4 × 1)-In undergoes a reversible phase transition below 120 K to an (8 × 2) structure, with a strong reduction of the density of states at the Fermi energy. From photoemission and scanning tunneling microscopy (STM) studies they concluded that this phase formed a 1D CDW system driven by a Peierls instability. These intriguing results provoked much experimental and theoretical work. However, the origin of the phase transition remains controversial. The phase transition cannot be based on a simple CDW model because only one of the metallic bands nests properly [3,15–19]. A triple-band Peierls instability has been suggested, where

an interband charge transfer modifies the Fermi surface to improve nesting [17], while a periodic lattice distortion that lowers the energy has also been suggested [6,9,10,20]. Recently, it has been proposed that, while the Peierls transition is important, other structural transitions are co-operatively involved [21].

Not only the mechanism of the (4 × 1) → (8 × 2) phase transition, but also the LT ground-state and its properties remain controversial. While the RT (4 × 1) phase is a quasi-1D metal [12,16,22], it has been variously suggested that the LT (8 × 2) phase is metallic, but with a lower density of states at the Fermi level [19,20,23], semimetallic [19], and semiconducting with a fundamental energy gap of 0.1–0.3 eV [15–18,21]. Most *ab initio* calculations predict the nanowire ground state to be characterized by the formation of In trimers (cf. Fig. 1) and find no gap opening [6,7,9,10]. Recently, however, a structure with In hexagons, resulting from shear distortions in neighboring chains (Fig. 1), has been predicted, which is semiconduct-
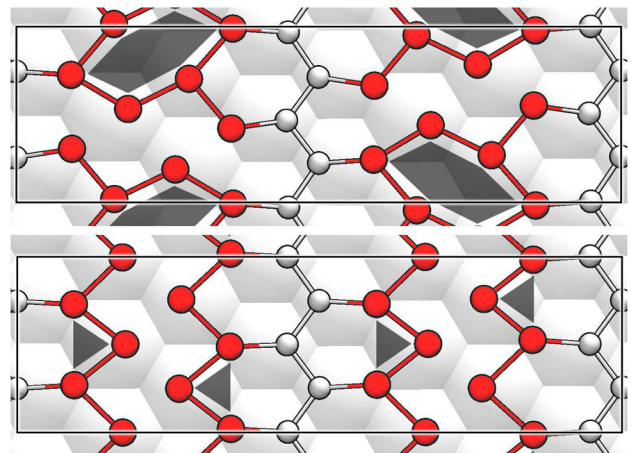

FIG. 1 (color online). Schematic top views of the hexagon and trimer model of the LT Si(111)-In nanowire array.

ing [24]. In Ref. [24] it was argued that the metallic RT phase arises from dynamic fluctuations between degenerate ground states, but recent photoemission [21] and Raman spectroscopy [11] results have cast doubt on this model. Total-energy calculations [13] of the hexagon and the trimer model for the LT phase concluded that an unambiguous identification of the internal structure of the ground state on energetic arguments is problematic. The energy differences between the competing structures are very small and depend on the approximations made in the calculations, e.g., the treatment of the In $4d$ states, and exchange and correlation effects. Cho and Lee [25] state that the hexagon model is not stable, but the model has been supported recently by positron diffraction studies [26].

Given these ambiguities, optical spectroscopic information from a new spectral region may be helpful. The small differences in geometry of the trimer and hexagon model lead to significant changes in the band structure near the Fermi level [13,24]. Direct optical transitions in this energy region, as probed by infrared spectroscopic ellipsometry (IRSE) and reflection anisotropy spectroscopy (RAS), are expected to be very sensitive to such changes.

In this Letter, we report the first measurements of optical excitation around the Fermi level for this system, in the mid-IR spectral range from 0.31 to 0.99 eV. We show that IRSE has submonolayer sensitivity in this spectral region and can discriminate between metallic and insulating electronic structures. In addition, the comparison of measured data with *ab initio* calculations provides strong evidence that excludes the trimer model and supports the hexagon model of the In nanowire ground state.

Vicinal, wedged n-type Si(111) samples offcut by 1° towards the $[\bar{1}\,\bar{1}\,2]$ direction were cleaned by heat treatment under ultrahigh vacuum (UHV), and a predominantly single domain Si(111)-(4 × 1)-In structure was grown by depositing In on the clean Si surface at 670 K. The surface order and the phase transition were monitored *in situ* with RAS, which has been shown to be very useful in monitoring the surface reconstructions of Si(111) [27]. The RAS measurements indicated that the dominant domain occupied about 80% of the surface. Further experimental details are reported elsewhere [28]. IRSE measurements [29,30] were made under UHV conditions using a photometric ellipsometer attached to a Bruker Vertex 70 series Fourier Transform Interferometer with a spectral resolution of 16 cm^{-1}. Ellipsometry measures the change of the polarization state upon reflection or transmission from the sample surface. The measurements were performed in reflection at 65° angle of incidence and the polarization state of the reflected radiation was analyzed [30]. The ellipsometric parameters, ψ and Δ, are related to the complex reflection coefficients for polarization perpendicular and parallel to the plane of incidence, r_s and r_p, by $r_p/r_s = \tan\psi \exp(i\Delta)$. In this Letter, only $\tan\psi$ was measured, as a sufficiently sensitive retarder was not available to measure

the phase difference Δ. Measurements of the clean Si surface at room temperature (RT) and at low temperature (LT) were used to normalize the In results presented in Figs. 2 and 3. A gap in the spectrum between 3600–3900 cm^{-1} is shown when the vibrational bands of atmospheric H_2O are significant. Measurements were made with the plane of incidence parallel to the In chains, along $[1\bar{1}0]$, and perpendicular to the chains, along $[\bar{1}\,\bar{1}\,2]$. These directions refer to the majority domain, but 20% of the surface is covered by two minority domains, rotated by 120°.

Figure 2 shows normalized IRSE spectra for the RT (4 × 1)-In and LT (8 × 2)-In phases, in the two orthogonal directions (the clean Si RT and LT spectra are shown at the bottom of the figure). The optical response is clearly anisotropic, particularly when allowing for the parallel contribution from the minority domains. There is a dramatic difference between the (4 × 1) and (8 × 2) phases in Fig. 2. The RT In-Si (4 × 1) metallic phase shows a low energy Drude-like tail and no interband transitions below 1 eV. This is in contrast to the behavior above 1 eV, where the response of the (4 × 1) structure is dominated by interband transitions [31,32]. The larger Drude-like response parallel to the chains arises from their highly anisotropic polarizabilities [27] and is consistent with the anisotropic conductivity of this surface, as measured by four-point probe STM [12,16]. The spectra show that IRSE can detect anisotropic metallic behavior at submonolayer coverages.

Three main observations can be made about the LT (8 × 2) spectra: (i) the spectral weight at low energy reduces dramatically, (ii) two peaks appear at 4015 ± 10 cm^{-1} (0.498 ± 0.002 eV) and 5800 ± 10 cm^{-1} (0.719 ± 0.002 eV), and (iii) a very small feature appears, centered at 2850 ± 100 cm^{-1} (0.35 ± 0.01 eV). This region is en-
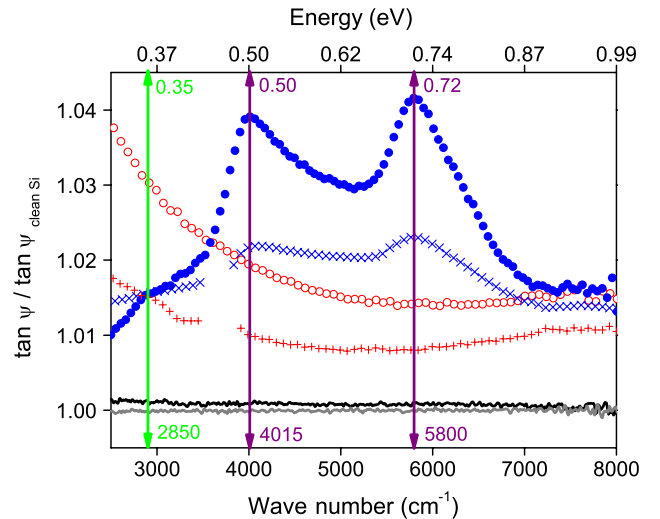

FIG. 2 (color online). IRSE spectra of the RT and LT In-Si phases, for planes of incidence parallel and perpendicular to the In chains: (4 × 1) parallel (○), (4 × 1) perpendicular (+), (8 × 2) parallel (●), (8 × 2) perpendicular (×). The clean Si spectra at 300 and 70 K are shown at the bottom.

larged in Fig. 3, where a linearly increasing background
has been subtracted in order to emphasize the peak, which
grows in intensity when the surface is cooled. Previous
high-resolution electron energy loss (HREELS) measure-
ments of the (8×2) phase, which showed three very
weak features at 0.35, 0.57, and 0.82 eV [20], are consistent
with the results reported here, given the poorer SNR of
HREELS at these higher energies. The small feature at
0.35 ± 0.01 eV agrees within error with the fundamental
gap of 0.30 ± 0.05 eV measured by STM [16]. The re-
moval of the low energy tail in the (8×2) phase, and its
replacement by two large peaks at 0.50 and 0.72 eV is new
evidence supporting a metal-insulator (MI) transition.
There is no evidence of residual metallic behavior in the
(8×2) phase in the mid-IR.

RAS is a powerful technique for probing optically an-
isotropic surface and interface structure [33], which mea-
sures the difference in reflectance, at near normal
incidence, of light linearly polarized in two orthogonal
directions at the surface plane. The response depends on
the imaginary part of the difference in the surface dielectric
function in the two orthogonal directions. For these
samples, the difference in reflectance parallel and perpen-
dicular to the chains is being measured. The IR data were
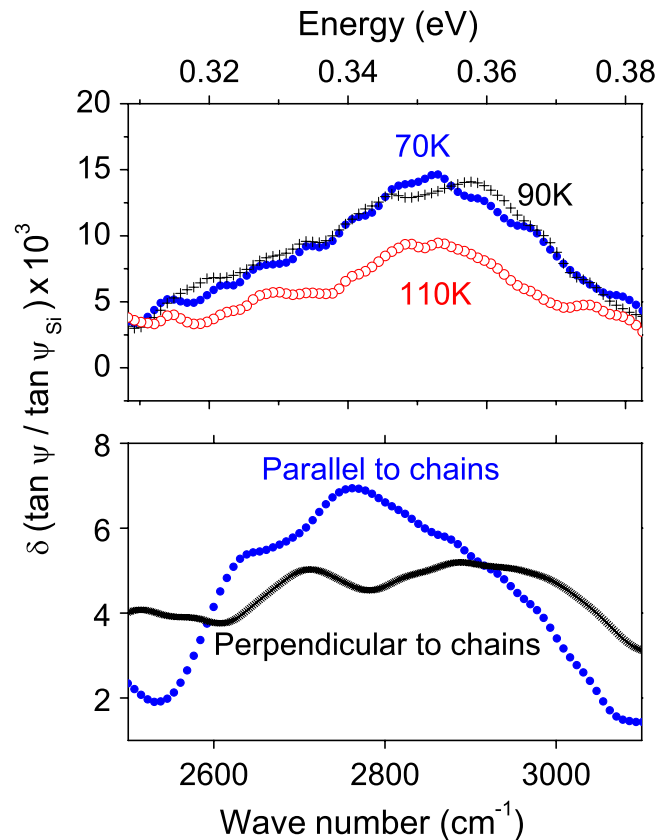measured with an InAs detector and the visible-UV data

with InGaAs and Si detectors, the changeover occurring at
0.75 eV.

Figure 4 shows measured and calculated RAS spectra.
The data reveal a smooth increase to low energy for the
RT (4×1) phase, while the LT (8×2) phase shows two
sharp positive peaks at 0.50 and 0.72 eV that correspond
exactly to the IRSE features discussed above. Positive
anisotropy indicates that optical transitions parallel to the
chains are dominant in this spectral region. Both phases
show the broader, negative 1.9 eV feature, which splits
below the MI transition [7,31,32].

The theoretical data are obtained using density func-
tional theory (DFT) within the local density approximation
(LDA) for exchange and correlation as implemented in
VASP [34]. The RAS is obtained from the slab polarizability
in the independent-particle approximation [32] and uses no
adjustable parameters. The calculated anisotropy of both
the trimer and hexagon models of the (8×2) structure
agree well with the experiment above 0.7 eV, as has been
reported previously [32]. Below 0.7 eV, only the hexagon
model looks similar to the experimental results. In particu-
lar, two positive peaks are predicted, separated by 0.24 eV.
This splitting agrees very well with the experimental split-
ting of 0.22 eV. The origin of the two peaks in the mid IR
can be traced to optical transitions close to the M point of
the surface Brillouin zone, indicated by P_1 and P_2/P_2' in
Fig. 5. Around M, nearly parallel valence and conduction
bands close to the Fermi level give rise to a high joint
density of states. From the orbital character of states (not
shown here) we can assign P_1 to transitions between
bonding and nonbonding In chain states within the single
In zigzag chains, while P_2 and P_2' involve in addition In-In
bonds between the two parallel zigzag chains. These bonds
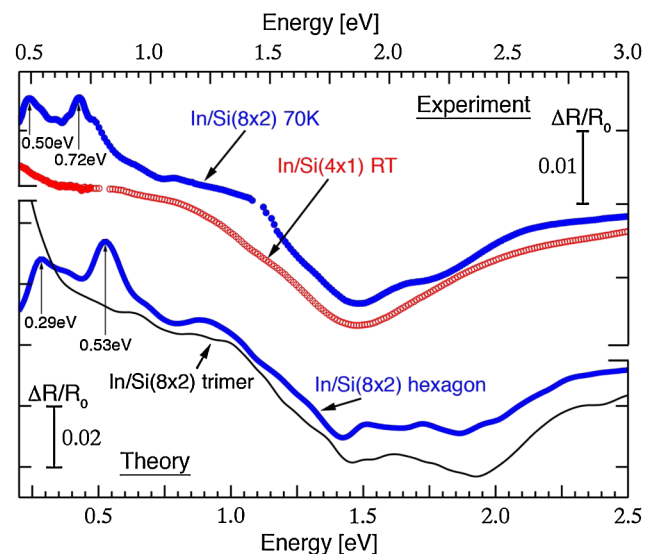are exclusively formed for the hexagon model (Fig. 1). The

FIG. 3 (color online).   Enlarged region for the (8×2) structure
from 2500 cm^{-1} to 3100 cm^{-1}, from which a linearly increasing
background has been subtracted. Upper figure: the effect of
cooling. Lower figure: the anisotropic response.

FIG. 4 (color online).   RAS spectra of Si(111)-(4 × 1)-In at
RT (300 K) and Si(111)-(8 × 2)-In at LT (70 K): upper, experi-
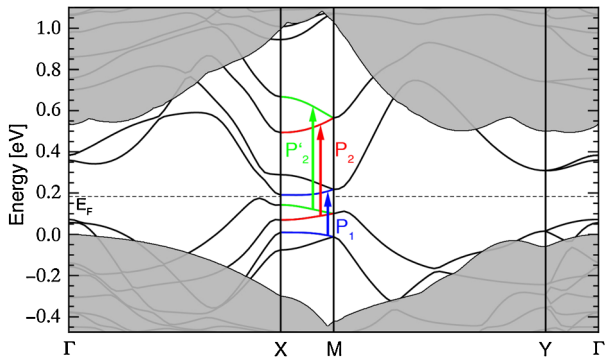ment; lower, theory. Note the different scales.

FIG. 5 (color online).   Band structure of the hexagon model for
Si(111)-(8 × 2)-In calculated within DFT-LDA. Pronounced op-
tical transitions showing up in the RAS spectra are marked. Gray
regions correspond to the projected Si bulk bands. The bulk
valence band maximum is chosen as energy zero. The Fermi
level is indicated.

spectra measured in the mid-IR are thus directly related to
the hexagon structure of the In nanowire array.

Detailed comparison reveals that the calculated mid-IR
peaks are redshifted by 0.25 eV (note the different scales in
Fig. 4). The underestimation of excitation energies is typi-
cal for DFT calculations where self-energy effects are
neglected. The complexity and size of the In nanowire
structure prevents the calculation of optical spectra using
many-body perturbation theory that includes self-energy
and excitonic effects [35]. Quasiparticle calculations for
the high-symmetry points of the hexagon model surface
band structure found self-energy effects to increase the
lowest transition energies by 0.26 eV on average [13]. A
larger shift of 0.5 eV, typical for Si excitation energies [35],
applies to the higher energy negative optical anisotropies,
because the optical transitions involve Si states [32].
Allowing for these energy shifts, the agreement between
the calculated and measured RAS spectra is truly
impressive.

In conclusion, the first mid-IR optical measurements and
ab initio calculations have been reported for the In-Si
nanowire system. IRSE has sufficient sensitivity to mea-
sure the optically anisotropic surface response of the In
chains on the metallic (4 × 1) surface. The dramatic shift
of spectral weight on cooling to form the (8 × 2) phase is
consistent with a MI phase transition. Strong, anisotropic
optical interband transitions were found with IRSE and
RAS at 0.50 and 0.72 eV for this phase. In contrast to the
trimer model, optical response calculations for the hexagon
model reproduced the measured features. In particular, the
0.7 eV peak arises from optical transitions involving the
additional In-In bonds that are only formed in the hexagon
model. These results provide strong evidence in favor of
the hexagon model of the In nanowire ground state.

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